Impact of metal impurities on solar cell performance

A.A.Istratov[(1)], T.Buonassisi[(1)], E.R.Weber[(2)], R.J.McDonald[(3)], A.R.Smith[(3)], R.Schindler[(4)], J.Isenberg[(4)], J.Kalejs[(5)], J.Rand[(6)], P.Geiger[(7)], G.Hahn[(7)], J.P.Rakotoniaina[(8)], and O.Breitenstein[(8)]

[(1)] University of California, LBNL, MS 62R203, 1 Cyclotron Road, Berkeley CA 94720, USA
[(2)] University of California, Dept. of Materials Science and Engineering, 374 Hearst Mining Building, Berkeley CA 94720, USA
[(3)] Lawrence Berkeley National Laboratory, MS 72R0150, 1 Cyclotron Rd., Berkeley, CA 94720, USA
[(4)] Fraunhofer Institute for Solar Energy Systems, Heidenhofstrasse 2, D-79110 Freiburg, Germany
[(5)] RWE Schott Solar, Inc., 4 Suburban Park Drive, Billerica, MA 01821-3980, USA
[(6)] Astropower, Solar Park, Newark, DE 19716-2000, USA
[(7)] University of Konstanz, Faculty of Physics, P.O.Box X916, D-78457 Konstanz, Germany
[(8)] Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany

ABSTRACT

Neutron activation analysis studies were performed to determine transition metal content in three types of multicrystalline material for solar cells: Astropower silicon-film sheet material, Baysix cast material, and EFG ribbon-grown mc-Si. The dominant metal impurities were found to be Fe, Ni, Co, Mo, and Cr. Copper was detected, but its concentration could not be accurately determined due to a very short decay time of the corresponding radioactive isotope. No substantial difference was observed between the metal content of the high and low lifetime areas of the same material. X-ray microprobe fluorescence spectrometry mapping of the shunt locations in Baysix and RGS material indicated presence of higher than average concentration of transition metals at certain shunt locations, thus indicating that metals can contribute to the shunt formation.

1. Introduction

The pace of commercialization of photovoltaics is determined by the cost of installed solar panels for the end-user. In order to make solar energy competitive, several low-cost production ribbon-growth or cast technologies were developed for high-volume production of multicrystalline silicon (mc-Si). Mc-Si is expected to have higher metal content than, e.g., Czochralski-grown silicon wafers because of lower requirements for the cleanliness of the production environment and possibly higher metal content of the feedstock. Additionally, the rapid silicon solidification rate does not allow metals to segregate in the melt. The trapped transition metals, which are known to be highly recombination active [1-3], may be one of the culprits of efficiency degradation of solar cells. Unfortunately, the data on metal content of multicrystalline silicon are scarce, and, to our knowledge, only two conclusive studies were published since 1993 [4, 5].

In this study, we apply two powerful tools, neutron activation analysis (NAA) and x-ray microprobe fluorescence spectroscopy (μ-XRF) to the analysis of metal content of solar cell materials, and discuss the potential impact of transition metals on solar cell efficiency.

2. Experimental

NAA studies were performed using three types of samples, Astropower Silicon-film sheet material, Baysix cast material, and EFG ribbon-grown mc-Si. EFG wafers were mapped with SPV in order to select samples with average (30-60 μm), lower than average (<20 μm), and higher than average (>80 μm) diffusion length. Baysix samples were cleaved from wafers from the bottom of the ingot (L_D=25-50 μm) and from the middle of the ingot (L_D=40-200 μm). Astropower samples were cut from two wafers, which were fully processed solar cells with stripped off front and back contacts. One of the two cells had better electrical properties than the other one.

The samples for analyses were chemically etched, weighed, wrapped in clean aluminum foil, irradiated at a nuclear reactor, unwrapped, etched again, and counted at a low background facility at Lawrence Berkeley National Laboratory.

μ-XRF analysis of shunts in solar cells were performed using Baysix and RGS material at Beamline 10.3.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory.

3. Results of neutron activation analysis

The main metal impurities found in the samples were Fe, Ni, Co, Cr, and Mo. Copper was also detected, but its concentration could not be determined accurately because of the short lifetime (12.7 hrs) of the corresponding radioactive isotope. Astropower samples had the highest overall metal concentration: 1.5×10^{16} cm^{-3} of iron, 1.8×10^{15} cm^{-3} of Ni, 9.7×10^{13} cm^{-3} of Co, 4.6×10^{13} cm^{-3} of Mo, 2×10^{13} cm^{-3} of W, and 4.8×10^{11} cm^{-3} of gold. Baysix material had somewhat lower metal concentration: 4×10^{14} cm^{-3} of Fe, 2.1×10^{13} cm^{-3} of Co, 1.0×10^{13} cm^{-3} of Cr, 1.5×10^{13} cm^{-3} of Mo, and 6.5×10^{10} cm^{-3} of Au. EFG wafers had the lowest metal concentration of the three materials: 6×10^{14} cm^{-3} of Fe, 1.7×10^{12} cm^{-3} of Co, 1.7×10^{12} cm^{-3} of Cr, 6.4×10^{12} cm^{-3} of Mo, and 2×10^{10} cm^{-3} of Au.

Analysis of samples of the same type of material cleaved from the areas with high and low minority revealed that only gold was found in 1.5 to 5 times higher concentrations in the low lifetime samples than in the high lifetime samples of all three materials. The rest of the metals detected by NAA showed either no trend at all, or, in some cases, were even found in slightly higher concentration in the areas with a higher diffusion length.

On the other hand, the total transition metal concentrations observed in all three mc-Si materials are much higher than would be sufficient to limit the minority carrier diffusion length at approximately 60 microns, typical for mc-Si, if these metals were in interstitial or substitutional state. For example, only approximately 2×10^{13} cm^{-3} of FeB pairs, or 2×10^{12} cm^{-3} of interstitial iron is sufficient to reduce the diffusion length to 50 microns [2]. Since the average metal concentration in mc-Si was found to be much higher than that, one may conclude that either transition metals are present in relatively recombination inactive chemical/structural state, or extremely inhomogeneously distributed in the wafer, or both. In either case, only a small fraction (anywhere between 1% and 10%) of the total metal concentration controls the minority carrier diffusion length, along with other structural defects which may also be recombination active. A small variation in the chemical/structural state of metals which leads to a change in their recombination properties may account for the different between “good” and “bad” grains in solar cells, regardless of the total metal content of these grains.

4. Analysis of metal content at shunt locations

The analyses discussed in this section were performed using RGS and Baysix solar cells, pre-characterized with lock-in thermography and LBIC. The location of shunts determined by lock-in thermography was superimposed on minority carrier diffusion length features observed in LBIC. Then the LBIC map was correlated with XBIC [6] maps in order to find the area of the shunt to scan with μ-XRF. Special precautions were taken to select only the shunts which are not caused by mechanical damage of the surface or defects at the edges of the cells.

Two types of mc-Si were analyzed, Baysix and RGS. In Baysix samples, we found clusters of silver with a small fraction of titanium. Since these metals are used for fabrication of contact strips on top of the wafers, we suggested that these shunts could be caused by unintentional contamination introduced during processing the contact strips.

Shunts in RGS solar cells had a different nature. Iron and copper were found at the shunt location, which coincided with so-called current collecting channels. It was reported in literature [7] that current collecting channels may cause local conductivity type inversion, thus extending the p-n junction into the depth of the wafer. Agglomeration of metals at these channels may increase the generation-recombination currents in the depletion region of the p-n junction and increase or even cause the shunting activity. Hence, our studies indicate that transition metals can play an important role in different types of shunting mechanisms.

5. Conclusions

High metal content of multicrystalline silicon indicates that metals may play an important, if not decisive, role in limiting the minority carrier diffusion length in silicon. Approximately equal concentration of metals found in low and high diffusion length areas of the same type of material proves that recombination properties of metals are determined primarily by their chemical/structural state. In order to getter or passivate these metals, it is essential to know where these metals are located in the solar cells, and how they can be transformed from more recombination active to less recombination active state, e.g., by a specific heat treatments, hydrogenation, etc.

Gettering remains an important means of reducing metal concentration. However, since one has to deal with a variety of metals present in concentrations of up to 10^{15} cm^{-3}, including those with low diffusion coefficients, one has to use high gettering temperatures combined with long gettering anneals to allow all these metal clusters to dissolve and diffuse to the gettering layer.

The presence of Fe, Ni, and Cr in all three types of materials, and the fact that the relative concentration of these metals is similar to that of stainless steel, may indicate that some of the metal contamination in solar cells stems from stainless steel.

Detection of increased metal concentration at shunts in RGS and Baysix solar cells indicates that metals may contribute to the shunt formation through diverse mechanisms.

6. Acknowledgements

The authors would like to acknowledge support from NREL, subcontract AAT-2-31605-03, and AG-Solar project of the government of Northrhein-Westfalia (NRW).

REFERENCES

1. A. Rohatgi, J. R. Davis, R. H. Hopkins, and P. G. McMullin, "A study of grown-in impurities in silicon by deep-level transient spectroscopy", *Sol. St. Electron.* **26**, 1039 (1983).
2. A. A. Istratov, H. Hieslmair, and E. R. Weber, "Iron contamination in silicon technology", *Appl. Phys. A* **70**, 489 (2000).
3. J. H. Reiss, R. R. King, and K. W. Mitchell, "Characterization of diffusion length degradation in Czochralski silicon solar cells", *Appl. Phys. Lett.* **68**, 3302 (1996).
4. A. Huber, G. Böhm, and S. Pahlke, "Industrial applications of instrumental neutron activation analysis", *J. Radioanal. Nucl. Chem.* **169**, 93 (1993).
5. D. Macdonald, A. Cuevas, A. Kinomura, and Y. Nakano, "Phosphorus gettering in multicrystalline silicon studied by neutron activation analysis", in *29th Photovoltaic Specialists Conference*, IEEE, New Orleans, LA (2002).
6. O. F. Vyvenko, T. Buonassisi, A. A. Istratov, H. Hieslmair, A. C. Thompson, R. Schindler, and E. R. Weber, "X-Ray Beam Induced Current (XBIC) - a synchrotron radiation based technique for the in-situ analysis of recombination properties and chemical nature of metal clusters in silicon", *J.Appl.Phys.* **91**, 3614 (2002).

7. O. Breitenstein, M. Langenkamp, and J. P. Rakotoniaina, "EBIC investigation of a 3-dimensional network of inversion channels in solar cells on silicon ribbons", *Solid State Phenom.* **78-79**, 29 (2001).